

Thermal effects and evolution of the defect concentration based on shear modulus relaxation data in a Zr-based metallic glass

Qi Hao(郝奇), Ji-Chao Qiao(乔吉超), E V Goncharova, G V Afonin, Min-Na Liu(刘敏娜), Yi-Ting Cheng(程怡婷), V A Khonik

Citation: Chin. Phys. B . 2020, 29(8): 086402 . **doi:** 10.1088/1674-1056/ab969c
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Effect of Sn and Al additions on the microstructure and mechanical properties of amorphous Ti-Cu-Zr-Ni alloys

Fu-Chuan Chen(陈福川), Fu-Ping Dai(代富平), Xiao-Yi Yang(杨霄熠), Ying Ruan(阮莹), Bing-Bo Wei(魏炳波)
Chin. Phys. B . 2020, 29(6): 066401 . **doi:** 10.1088/1674-1056/ab8628

Effect of Ni substitution on the formability and magnetic properties of $Gd_{50}Co_{50}$ amorphous alloy

Ben-Zheng Tang(唐本镇), Xiao-Ping Liu(刘晓萍), Dong-Mei Li(李冬梅), Peng Yu(余鹏), Lei Xia(夏雷)
Chin. Phys. B . 2020, 29(5): 056401 . **doi:** 10.1088/1674-1056/ab7da8

Secondary relaxation and dynamic heterogeneity in metallic glasses: A brief review

J C Qiao(乔吉超), Q Wang, D Crespo, Y Yang(杨勇), J M Pelletier
Chin. Phys. B . 2017, 26(1): 016402 . **doi:** 10.1088/1674-1056/26/1/016402

Interstitialcy theory of condensed matter states and its application to non-crystalline metallic materials

V A Khonik
Chin. Phys. B . 2017, 26(1): 016401 . **doi:** 10.1088/1674-1056/26/1/016401

Decline of nucleation in the heating process with a high heating rate

Yang Gao-Lin, Lin Xin, Song Meng-Hua, Hu Qiao, Wang Zhi-Tai, Huang Wei-Dong
Chin. Phys. B . 2014, 23(8): 086401 . **doi:** 10.1088/1674-1056/23/8/086401

RAPID COMMUNICATION

Thermal effects and evolution of the defect concentration based on shear modulus relaxation data in a Zr-based metallic glass*

Qi Hao(郝奇)[1], Ji-Chao Qiao(乔吉超)[1,†], E V Goncharova[2], G V Afonin[2], Min-Na Liu(刘敏娜)[1], Yi-Ting Cheng(程怡婷)[1], and V A Khonik[2]

[1] School of Mechanics, Civil Engineering and Architecture, Northwestern Polytechnical University, Xi'an 710072, China
[2] Department of General Physics, Voronezh State Pedagogical University, Lenin Street 86, Voronezh 394043, Russia

(Received 8 April 2020; revised manuscript received 8 May 2020; accepted manuscript online 27 May 2020)

A relationship between thermal effects and relaxation of the high-frequency shear modulus upon heat treatment of bulk $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ metallic glass is found. This relationship is attributed to the relaxation of a interstitial-type defect system frozen-in from the melt upon glass production. Calorimetric data show that thermal effects occurring on heating include heat release below the glass transition temperature, heat absorption above it and heat release caused by crystallization. The equation derived within the Interstitialcy theory can be used to calculate the shear modulus relaxation using the calorimetric data. The obtained results are used to trace the defect concentration as functions of temperature and thermal prehistory.

Keywords: shear modulus, metallic glass, structural relaxation, interstitialcy theory

PACS: 64.70.pe, 07.20.Fw, 61.43.Dq **DOI:** 10.1088/1674-1056/ab969c

1. Introduction

Elastic moduli, which essentially reflect interatomic forces, constitute key physical parameters of metallic glass. In particular, an important but still unresolved problem is why the shear modulus G and Young's modulus E of metallic glasses are reduced by about 20% to 40% as compared with the maternal crystalline state.[1] It is believed that this phenomenon is related to the structural heterogeneity or internal defects of metallic glasses.[2] In fact, the microstructural heterogeneity of metallic glass has been extensively investigated in recent years.[3–5] It should be emphasized that the shear modulus is tightly related to the structural origin of plastic deformation and glass transition in metallic glasses.[6–8] In recent years, many investigations were focused on correlations among the shear modulus, glass forming ability, glass transition and mechanical properties of metallic glasses.[2,9–11]

On the other hand, the shear modulus is an important physical parameter of the Interstitialcy theory (IT) proposed by Granato.[10,12] The theory is based on an experimental observation that interstitial defects produced by soft neutron irradiation at $T = 4$ K result in a sharp decrease of the shear modulus of single crystalline Cu.[13] The extrapolation of these experimental data shows that the shear modulus should drop to nearly zero if the concentration of interstitial defects can reach 2% to 3%. Meanwhile, it is known that a vanishing shear modulus is a signature of liquids.[13] Although interstitial defects in crystalline materials can be understood as two atoms trying to occupy the same lattice position, these defects do not have such a clear geometric structure in amorphous materials. However, it is still considered that the interstitial defects in glass retain their basic characteristics in the crystalline state, such as high sensitivity to the external shear stress, specific low-frequency vibration modes and high vibrational entropy.[14,15] These defects remain identifiable structural units in the melt becoming frozen in solid glass upon melt quenching. Diverse relaxation phenomena occurring upon structural relaxation and crystallization in metallic glasses can be quantitatively attributed to thermoactivated changes of the defect concentration.[16,17] It is important, therefore, to trace how this quantity changes due to different heat treatment procedures.

Within the framework of the Interstitialcy theory, the shear modulus of a metallic glass is determined by the shear modulus μ of maternal crystal (i.e., the one used for glass production) and the defect concentration c,[12]

$$G = \mu \exp(-\alpha\beta c), \tag{1}$$

where β is a dimensionless shear susceptibility (usually 15–25 in metallic glasses) and a dimensionless parameter $\alpha \approx 1$ is related to the defect strain field.[16] A decrease or increase of the defect concentration (depending on temperature and/or thermal prehistory) results in the corresponding relatively big (due to the big β) changes of the shear modulus. Therefore, it

*Project supported by the National Natural Science Foundation of China (Grant No. 51971178), the Astronautics Supporting Technology Foundation of China (Grant No. 2019-HT-XG), the Natural Science Foundation of Shaanxi Province, China (Grant No. 2019JM-344), the Russian Science Foundation (Grant No. 20-62-46003), and the Fundamental Research Funds for the Central Universities, China (Grant Nos. 3102019ghxm007 and 3102017JC01003).

†Corresponding author. E-mail: qjczy@nwpu.edu.cn

© 2020 Chinese Physical Society and IOP Publishing Ltd

is possible to probe interstitial-type defects in metallic glasses with the help of the shear modulus study. Combined with another key equation of the IT, $H = \alpha\Omega G$, which states that the defect formation enthalpy H is proportional to the shear modulus, where Ω is the volume per atom, this approach leads to an expression for the heat flow caused by a change of the defect concentration, i.e.,

$$W = \frac{\dot{T}}{\beta\rho}\left[\frac{G}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}T} - \frac{\mathrm{d}G}{\mathrm{d}T}\right], \tag{2}$$

where ρ is the density, which is assumed to be constant upon heating, $\dot{T}$ is the heating rate.[16,18] According to Eq. (2), the heat flow is determined by temperature derivatives of the shear modulus of glass and maternal crystal. Using this equation, the heat release and heat absorption of metallic glass during structural relaxation and crystallization can be calculated.[18–21] The purpose of the this work is to reconstruct the temperature dependence of the shear modulus from differential scanning calorimetry (DSC) measurements using the IT as a theoretical background and discuss the evolution of interstitial-type defect system assumed to be responsible for the heat effects and shear elasticity.

2. Experimental procedure

In the present study, model glassy $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ (at.%) prepared by melt suction technique was selected for the investigation. The glassy nature of samples was confirmed by x-ray diffraction (XRD, Rigaku D/max 2500 X). Thermal properties were determined by differential scanning calorimetry (Hitachi DSC 7020) carried out in flowing high purity N_2 at a heating rate of 3 K/min.

Electromagnetic acoustic transformation (EMAT) method was used for the high-frequency f (≈600–700 kHz) shear modulus measurements of 5 mm×5 mm×2 mm samples. In this method, transverse vibration of a sample is excited as a result of the Lorentz interaction of external magnetic field and surface current of a metallic sample.[22] The relative error in frequency measurements was estimated to be about 100 ppm near the glass transition temperature T_g and by an order of magnitude smaller well below T_g.[19] The shear modulus was calculated by $G(T) = G_{rt}f^2(T)/f_{rt}^2$, where f_{rt} and $G_{rt} \approx 33.8$ GPa[23] are the transverse vibration frequency and shear modulus at room temperature, respectively. Density change due to structural relaxation and crystallization (≈ 1% at most) is not considered when calculating the shear modulus in this way. The heating rate of shear modulus measurements is the same as that of the DSC measurements, 3 K/min.

3. Results and discussion

3.1. Reconstruction of shear modulus based on DSC data

Integrating Eq. (2) from room temperature T_{rt} to a temperature T, the shear modulus $G(T)$ can be expressed as[14]

$$G(T) = \frac{G_{rt}}{\mu_{rt}}\mu(T) - \frac{\rho\beta}{\dot{T}}\int_{T_{rt}}^{T} W(T)\mathrm{d}T, \tag{3}$$

where the shear moduli of glass G_{rt} and crystal μ_{rt} at room temperature as well as the heat flow $W(T)$ can be obtained via EMAT and DSC measurements, respectively. This equation can be used to calculate temperature dependence of the shear modulus in the initial and relaxed states and the results can be then compared with the experimental data.

Figure 1 shows the results of DSC measurements. Runs 1, 2, and 3 are the DSC curves in the initial state, relaxed state (obtained by heating up to 715 K, deep in the supercooled liquid state), and crystalline state (produced by heating up to 870 K), respectively. Glass transition temperature $T_g = 692$ K is defined in the inset of Fig. 1. The heat flows of initial (red squares) and relaxed (blue triangles) samples were calculated by $W_{ini} = W_{run1} - W_{run3}$ and $W_{rel} = W_{run2} - W_{run3}$, respectively.

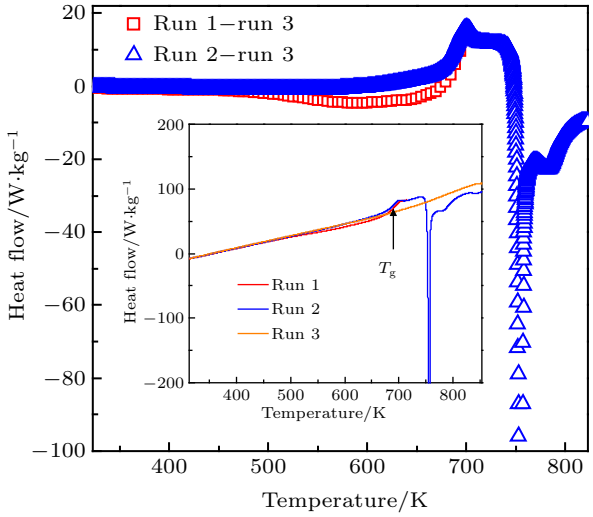


Fig. 1. The heat flows for the initial and relaxed samples after the subtraction of the heat flow for the fully crystallized state (labelled (difference between runs 1 and 3) and (difference between runs 2 and 3), respectively). The inset shows DSC curves of the $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ bulk metallic glass in the initial state (run 1), relaxed state obtained by preheating up to 715 K (run 2) and after the full crystallization (run 3).

Figure 2 gives temperature dependences of the shear modulus of glassy $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ in the initial (red squares) and relaxed (blue triangles) states. In the initial state (run 1), the shear modulus decreases almost linearly up to a temperature of about to 500 K due to the anharmonicity. Upon continued heating, a linear shear modulus decrease is superimposed by its slight increase (over the dotted line) due to structural relaxation in the range 500 K $\leqslant T \leqslant$ 690 K. Above the glass transition temperature T_g, the shear modulus starts to decrease sharply. In the relaxed state (run 2), relaxation-induced

shear modulus increase occurring during run 1 disappears. It is worth mentioning that the shear modulus curves in the initial and relaxed states (run 1 and run 2) merge at $T > T_g$. In the crystalline state (run 3), the shear modulus μ decreases linearly with temperature without distinct features. In general, the shear modulus behavior described above is similar to the results obtained on other metallic glasses.[24,25]

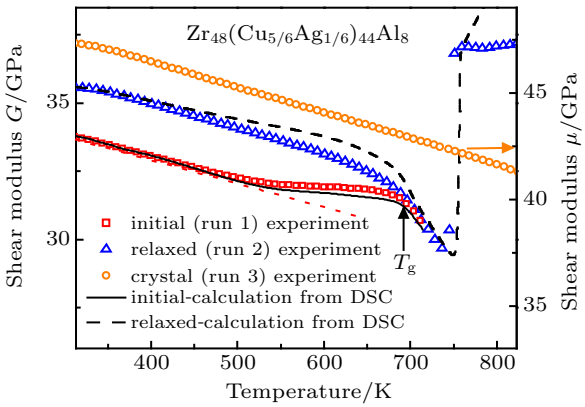


Fig. 2. Temperature dependence of the shear modulus of $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ bulk metallic glass in the initial, relaxed and crystalline states measured at a heating rate of 3 K/min. The black solid and dashed curves are calculated using Eq. (3), in good agreement with the experimental data.

Figure 2 also gives the calculated temperature dependences of the shear modulus in the initial and relaxed states using Eq. (3) (black solid and black dashed curves, respectively). Room-temperature shear moduli used in the calculation for the initial, relaxed, and crystalline states were accepted (according to the corresponding resonant frequency changes) to be 33.80 GPa, 35.59 GPa, and 47.38 GPa, respectively. The shear susceptibility and the density (considered constant) were taken to be 19 and 7.1 g/cm^3, respectively.[23] It is seen that the experimental results are in good accordance with the prediction of the IT given by Eq. (3). In particular, the calculation reproduces (i) structural relaxation-induced increase of the shear modulus in the initial state below T_g, which disappears after relaxation is completed (run 2), (ii) rapid decrease of the shear modulus above T_g in the supercooled liquid state, and (iii) fast G-increase upon continued heating due to the crystallization. These facts provide the evidence that the origin of shear modulus changes are related to the modification of the interstitial-type defect structure as sketched above.

3.2. Evolution of the defect concentration derived from temperature dependence of the shear modulus

The agreement between the experimental and calculated shear modulus data shown in Fig. 2 implies that the IT can be used for further data analysis. With the basic Eq. (1) of the IT, one can relate changes of the shear modulus with the defect concentration. First, taking the logarithm and calculating the derivative over the temperature, one arrives at

$$\alpha\beta \frac{\mathrm{d}c}{\mathrm{d}T} = \frac{\mathrm{d}}{\mathrm{d}T} \ln \frac{\mu}{G}. \tag{4}$$

This equation shows that the derivative in the right indicates the way of the defect structure changing: if this derivative is negative then the defect concentration will decrease and vice versa. This prediction can be verified using the experimental shear modulus data shown in Fig. 2.

Figure 3 gives the temperature dependence of the derivative $\mathrm{d}\ln(\mu/G)/\mathrm{d}T$ for the initial state (red squares) and relaxed state (blue triangles). It is seen that this derivative is close to zero in the initial state at temperatures ranging from room temperature to 500 K, indicating almost constant defect concentration (see below). At intermediate temperatures (500 K to 690 K), a negative value of the derivative $\mathrm{d}\ln(\mu/G)/\mathrm{d}T$ in the initial state corresponds to a reduction in the defect concentration due to structural relaxation. A small part of the elastic energy stored by interstitial-type defects is released as heat during this process. In the supercooled liquid region, the defect concentration increases rapidly.

In the relaxed state, the right-hand side of Eq. (4) is always positive (see Fig. 3) and increases with temperatures above 580 K, indicating a rise of the defect concentration. It is worth noting that the derivatives $\mathrm{d}\ln(\mu/G)/\mathrm{d}T$ for initial and relaxed states are almost zero at temperature below 500 K. This leads to a conclusion that temperature coefficients of shear moduli for the glassy state in the absence of structural relaxation and crystalline state are equal, in line with earlier observations.[17]

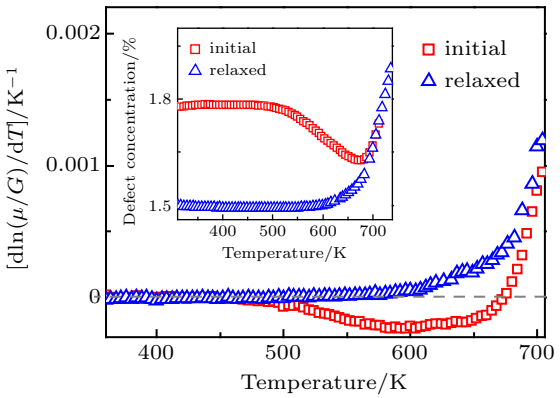


Fig. 3. Temperature dependence of the derivative $\mathrm{d}\ln(\mu/G)/\mathrm{d}T$ for the initial (red squares) and relaxed states (blue triangles). Positive and negative values of this derivative correspond to an increase and decrease of the defect concentration, respectively, as implied by Eq. (4). This is directly seen when compared with the inset, which shows temperature dependences of the defect concentration in the initial and relaxed states calculated using Eq. (5), see the text for more details.

Equation (1) can also be rewritten as

$$c = \frac{1}{\alpha\beta} \ln \frac{\mu}{G}. \tag{5}$$

This equation can be used for a direct calculation of the defect concentration, as shown in the inset of Fig. 3. It is seen that the

defect concentration in the initial state remains at an almost constant value of 1.8% at temperatures ranging from room temperature to 500 K. At intermediate temperatures (500 K to 690 K), the defect concentration decreases due to structural relaxation, which is accompanied by the heat release (see Fig. 1). Above T_g, the defect concentration increases rapidly with temperature because of the approaching to the metastable equilibrium state. It can be noted that the defect concentration in the relaxed state at room temperature is by about 0.3% smaller as compared with the initial state. It is this defect concentration decrease that is accompanied by the exothermal reaction. The origin of this heat release can be ascribed to the dissipation of the elastic energy related to the defects. It is also worth mentioning that a decrease of the defect concentration in the relaxed state due to structural relaxation below T_g is absent, as one would naturally expect. Thus, measurements of the shear modulus provide an effective tool for the monitoring of the defect concentration.

4. Conclusion

In this work, we show that temperature dependence of the shear modulus of $Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$ metallic glass can be quantitatively predicted by using calorimetric data. This fact provides the evidence that the origin of structural relaxation can be related to a thermoactivated change of the concentration of interstitial-type defects assumed to be responsible for the relationship between the shear modulus and heat effects. Upon heating the initial glass, the defect concentration first decreases due to structural relaxation below T_g, which is accompanied by the heat release. This effect disappears in the relaxed state obtained by heating into the supercooled liquid state. Upon approaching T_g, the defect concentration start to rapidly increase both in the initial and relaxed state leading to the heat absorption. Heat release is determined by the release of the total formation enthalpy of the defects disappeared upon structural relaxation below T_g. Heat absorption near and above T_g corresponds to the absorption of the total formation enthalpy of defects generated at these temperatures. All these physical processes are reflected in the changes of the shear modulus of glass. The latter constitutes a major thermodynamic parameter of metallic glass structure.

References

[1] Golding B, Bagley B G and Hsu F S L 1972 *Phys. Rev. Lett.* **29** 68
[2] Wang W H 2012 *Prog. Mater. Sci.* **57** 487
[3] Hou Z Y, Liu R S, Tian Z A and Wang J G 2011 *Chin. Phys. B* **20** 66102
[4] Yang L and Guo G Q 2010 *Chin. Phys. B* **19** 126101
[5] Qiao J C, Wang Q, Crespo D, Yang Y and Pelletier J M 2017 *Chin. Phys. B* **26** 16402
[6] Schuh C A, Hufnagel T C and Ramamurty U 2007 *Acta Mater.* **55** 4067
[7] Wang W H 2012 *Nat. Mater* **11** 275
[8] Wagner H, Bedorf D, Küchemann S, Schwabe M, Zhang B, Arnold W and Samwer K 2011 *Nat. Mater* **10** 439
[9] Rouxel T, Ji H, Hammouda T and Moréac A 2008 *Phys. Rev. Lett.* **100** 225501
[10] Qiao J C, Yao Y, Pelletier J M and Keer L M 2016 *Int. J. Plast* **82** 62
[11] Qiao J C, Wang Q, Pelletier J M, Kato H, Casalini R, Crespo D, Pineda E, Yao Y and Yang Y 2019 *Prog. Mater. Sci.* **104** 250
[12] Granato A V 2014 *Eur. Phys. J. B* **87** 18
[13] Holder J, Granato A V and Rehn L E 1974 *Phys. Rev. Lett.* **32** 1054
[14] Makarov A S, Mitrofanov Y P, Afonin G V, Kobelev N P and Khonik V A 2019 *Scr. Mater.* **168** 10
[15] Goncharova E V, Konchakov R A, Makarov A S, Kobelev N P and Khonik V A 2017 *J. Phys.: Condens. Matter* **29** 305701
[16] Khonik V A and Kobelev N P 2019 *Metals* **9** 605
[17] Afonin G V, Mitrofanov Y P, Kobelev N P, da Silva Pinto M W, Wilde G and Khonik V A 2019 *Scr. Mater.* **166** 6
[18] Mitrofanov Y P, Makarov A S, Khonik V A, Granato A V, Joncich D M and Khonik S V 2012 *Appl. Phys. Lett.* **101** 131903
[19] Mitrofanov Y P, Wang D P, Makarov A S, Wang W H and Khonik V A 2016 *Sci. Rep.* **6** 23026
[20] Mitrofanov Y P, Afonin G V, Makarov A S, Kobelev N P and Khonik V A 2018 *Intermetallics* **101** 116
[21] Duan Y J, Qiao J C, Crespo D, Goncharova E V, Makarov A S, Afonin G V and Khonik V A 2020 *J. Alloys Compd.* **830** 154564
[22] Hirao M and Ogi H 2017 *Electromagnetic Acoustic Transducers* (Berlin: Springer)
[23] Jiang Q K, Wang X D, Nie X P, Zhang G Q, Ma H, Fecht H J, Bendnarcik J, Franz H, Liu Y G, Cao Q P and Jiang J Z 2008 *Acta Mater.* **56** 1785
[24] Makarov A S, Khonik V A, Wilde G, Mitrofanov Y P and Khonik S V 2014 *Intermetallics* **44** 106
[25] Makarov A S, Mitrofanov Y P, Konchakov R A, Kobelev N P, Csach K, Qiao J C and Khonik V A 2019 *J. NonCryst. Solids* **521** 119474